nature materials

SUPPLEMENTARY INFORMATION

DOI: 10.1038/NMAT4784

Charge-transport model for conducting polymers

Stephen Dongmin Kang[1,2] and G. Jeffrey Snyder[1,2]

[1] *Department of Applied Physics and Materials Science, California Institute of Technology, CA 91125, USA*
[2] *Department of Materials Science and Engineering, Northwestern University, IL 60208, USA*

1 Charge transport models analyzed using a transport function

Charge transport equations and models commonly cited in the literature can typically be reduced to a transport function $\sigma_E(E)$. Because the underlying picture or assumptions behind various equations are often not transparent, with the transport function approach it is easier to compare different models on a common basis. Here, we derive a variety of commonly used equations and models, clarifying what $\sigma_E(E)$ is in each model under which assumptions.

We start by elaborating on the transport function σ_E, which could be described as the capability for electrical conduction at each energy level in the units of electrical conductivity. It is not the actual contribution to conductivity at each energy level because electrons are Fermions and only the transport function near the chemical potential is utilized in charge transport (also see Section 1.6). Electrical conductivity is obtained through:

$$\sigma = \int \sigma_E \left(-\frac{\partial f}{\partial E}\right) dE, \tag{S1}$$

and the Seebeck coefficient is obtained through:

$$S = \frac{k_B}{e} \frac{\int \sigma_E \left(-\frac{\partial f}{\partial E}\right) \left(\frac{E-E_F}{kT}\right) dE}{\int \sigma_E \left(-\frac{\partial f}{\partial E}\right) dE}. \tag{S2}$$

These equations can be obtained from solving the Boltzmann transport equation[1–3]. By finding the form of σ_E and required assumptions that make Eq.S1 and S2 yield the equations for conductivity and Seebeck coefficient, respectively, of a given model, one can analyze and compare different charge transport models.

We note that, although we use the notation E_F (the subscript comes from "Fermi level"), it should be understood that we generally refer to the electron chemical potential[a] because we are interested in finite temperatures. When there is a transport edge E_t, the position of the chemical potential with respect to the transport edge $E_F - E_t$ is a relevant parameter which we define with $\eta = \frac{E_F - E_t}{k_B T}$ in reduced units[b]. η is referred to as the reduced chemical potential.

1.1 Mott's mobility edge model

Here we derive the functional form (rather than the physical model behind it) of the mobility edge transport model as given by Mott[3] using a transport function approach. Mott assumes the non-degenerate limit where $\eta \ll -1$, and describes the conductivity by:

$$\sigma = \sigma_{min} \exp\left(-\frac{E_t - E_F}{k_B T}\right), \tag{S3}$$

[a] Often interchangeably used with the term "Fermi level," which could also refer exclusively to the electron chemical potential at 0 K. The chemical potential at room temperature can be significantly different in doped polymers.

[b] The explicit use of reduced energy does not imply a particular temperature dependence of σ_E.

DOI: 10.1038/NMAT4784

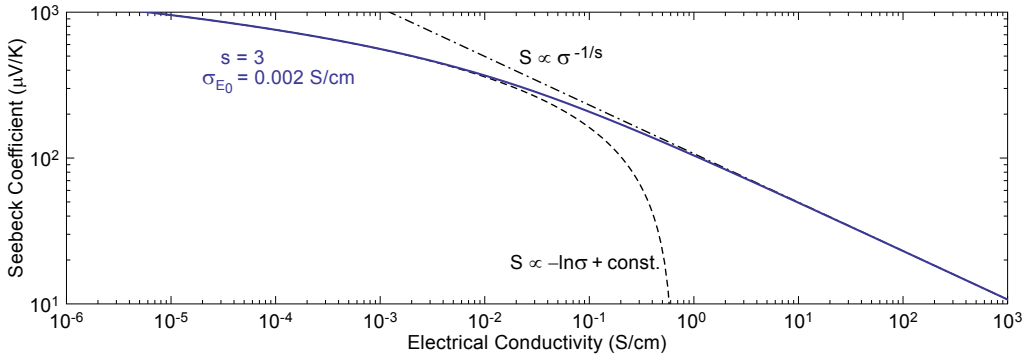

Figure S1: An example calculation showing how the equations in the non-degenerate and degenerate limits approximate the full calculation. The solid line is the full calculation using the noted parameters. The dashed line is from Eq.S8 and the dash-dot line is from Eq.S11.

where σ_{min} is the conductivity at the transport edge (corresponds to the mobility edge) in the 0 K limit[c]. Using our notation, we can simply write $\sigma = \sigma_{min}\exp(\eta)$. For the Seebeck coefficient, Mott gives:

$$S = \frac{k_B}{e}\left(\frac{E_t - E_F}{kT} + 1\right). \tag{S4}$$

From Eq.S3 and S4, the thermopower-conductivity relation is obtained:

$$S = \frac{k_B}{e}\left[1 - \ln\left(\frac{\sigma}{\sigma_{min}}\right)\right]. \tag{S5}$$

For the derivation, we start with the same transport function form as in the main text ($\sigma_E(E) = \sigma_{E_0}\cdot(E - E_t/k_BT)^s$). The non-degenerate assumption allows one to replace Fermi-Dirac statistics with Boltzmann statistics, which reduces the equation for conductivity (Eq.7 in main text) to:

$$\sigma = \sigma_{E_0}\cdot sF_{s-1}(\eta) \;\rightarrow\; \sigma_{E_0}s\Gamma(s)\exp(\eta) \quad (\eta \ll -1), \tag{S6}$$

and, similarly, the equation for Seebeck coefficient (Eq.8 in main text) to:

$$S = \frac{k_B}{e}\left[\frac{(s+1)F_s(\eta)}{sF_{s-1}(\eta)} - \eta\right] \;\rightarrow\; \frac{k_B}{e}\left[s + 1 - \eta\right] \quad (\eta \ll -1). \tag{S7}$$

The combination yields the thermopower-conductivity relation:

$$S = \frac{k_B}{e}\left[s + 1 - \ln\left(\frac{\sigma}{\sigma_{E_0}s\Gamma(s)}\right)\right] \quad (\eta \ll -1). \tag{S8}$$

This equation is valid in the non-degenerate limit ($\eta \ll -1$) where there is a transport edge E_t below which there is no contribution to conduction. It is seen from comparison that $s = 0$ (*i.e.* constant transport function above the mobility edge; see Fig.1d of main text or Fig.S3) is assumed by Mott in his model (note that $\lim_{s\to 0} s\Gamma(s) \to 1$), which we showed in the main text to be not suitable for describing many conducting polymer samples. We note that the Arrhenius temperature dependency of conductivity $\sigma \propto \exp(\eta)$ in Mott's model is a result of the chemical potential being far below the transport edge (or the mobility edge).

Mott's relation between thermopower and conductivity ($S \propto -\ln\sigma + const$) does hold regardless of the transport exponent s when in the $\eta \ll -1$ limit, as shown in Fig.S1. However, this relation only requires the existence of a transport edge; it does not necessarily require the

[c]Although we keep the original notation of σ_{min} here, it should not be considered an actual minimum. See Mott's account in [4].

physical picture Mott uses. One should not interpret σ_{min} or $\sigma_{E_0} \cdot s\Gamma(s)$ with Mott's model just based on an agreement of the $S - \sigma$ relation in the $(\eta \ll -1)$ limit.

Because of the relation $S \propto -\ln\sigma + const$ in the non-degenerate limit, traditionally $S - \sigma$ plots are done on a linear S and log σ scale (Jonker plot, Fig.S2). This approach could be helpful when investigating lightly-doped samples.

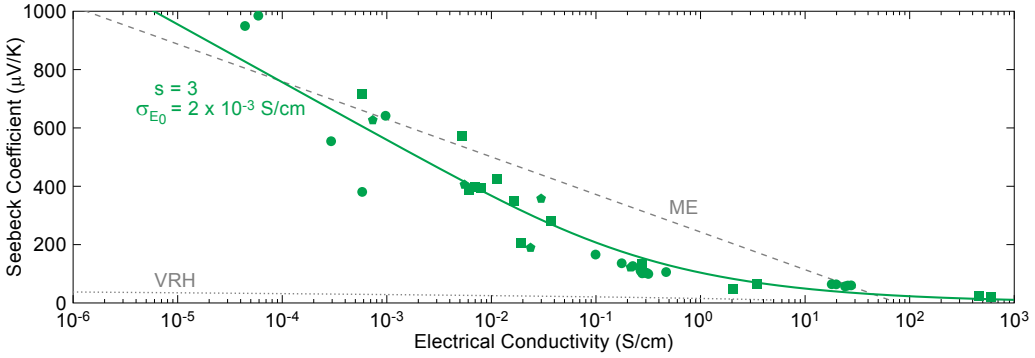

Figure S2: A Jonker plot of the data in Fig.3a of the main text. The linear portion of the full calculation curve (solid line) shows the non-degenerate limit. Mott's mobility edge model (ME) as estimated in Ref.[5] (dashed line) shows a different slope than that found in the non-degenerate limit because it was attempted to fit the entire data range. Mott's variable range hopping (VRH) model also from Ref.[5] is shown for comparison (dotted line).

1.2 The $S \propto \sigma^{-1/s}$ relation

An inverse power law relation $S \propto \sigma^{-1/s}$ between thermopower and conductivity has been found empirically in Ref.[5]. This relation can be explained using $\sigma_E(E) = \sigma_{E_0} \cdot (E - E_t/k_BT)^s$ in the degenerate limit $(\eta \gg 1)$. By setting $E_t = 0$ and doing a Sommerfeld expansion, conductivity becomes:

$$\sigma = \sigma_{E_0} \int_0^\infty \left(\frac{E}{k_BT}\right)^s \left(-\frac{\partial f}{\partial E}\right) dE \;\rightarrow\; \sigma_{E_0}\eta^s \quad (\eta \gg 1), \tag{S9}$$

and the Seebeck coefficient becomes:

$$S = \frac{k_B}{e}\frac{\sigma_{E_0}}{\sigma} \int_0^\infty \left(\frac{E}{k_BT} - \eta\right)\left(\frac{E}{k_BT}\right)^s \left(-\frac{\partial f}{\partial E}\right) dE \;\rightarrow\; \frac{k_B}{e}\frac{\pi^2}{3} s\eta^{-1} \quad (\eta \gg 1). \tag{S10}$$

By combining Eq.S9 and S10, we can obtain the thermopower-conductivity relation:

$$S = \frac{k_B}{e}\frac{\pi^2}{3} s \left(\frac{\sigma}{\sigma_{E_0}}\right)^{-1/s} \quad (\eta \gg 1) \tag{S11}$$

which gives the simple scaling relation $S \propto \sigma^{-1/s}$. A comparison to the full calculation is shown in Fig.S1. Note from this figure that, for the case of $s = 3$, fittings with Eq.S11 are best done at $S < 200$ μV/K.

In Ref.[5], the empirical relation was fit as $S \propto \sigma^{-1/4}$. Since $S \propto \sigma^{-1/s}$ only holds in the degenerate limit in our model, $s = 3$ gives a fit superior to $s = 4$ for the entire range of data. The $\sigma^{-1/4}$ is approximately the average slope around the transport edge for the $s = 3$ model.

1.3 Heikes formula for narrow transport functions

The Heikes formula[6] (or sometimes referred to as the Mott-Heikes formula) is commonly cited to describe insulators, amorphous materials, or polaron conductors:

$$\sigma = \sigma_M \cdot c(1 - c) \tag{S12}$$

DOI: 10.1038/NMAT4784

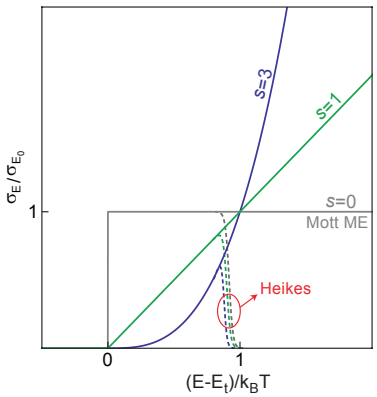

Figure S3: The transport function σ_E of the Heikes equations, where a narrow function close to the transport edge $E - E_t < k_BT$ is assumed regardless of the functional form. The transport function and energy axes are normalized with the transport coefficient σ_{E_0} and k_BT, respectively.

$$S = \frac{k_B}{e} \ln\left(\frac{1-c}{c}\right), \tag{S13}$$

where c is the fraction of carriers that are available at the transport energy level or narrow band and σ_M is a constant. A closely related equation for the Seebeck coefficient is:

$$S = \frac{E_t - E_F}{eT}. \tag{S14}$$

In our convention, this equation is equivalent to $S = (k_B/e) \cdot (-\eta)$.

Here we clarify the assumptions behind these equations by deriving it using the transport function σ_E. The key is to assume that the transport function is nonzero only in a narrow range (compared to k_BT) around E_t such as a narrow band. It follows that any function that does not vary much in a range of k_BT (such as the Fermi-Dirac distribution function) can be considered a constant value within that narrow range:

$$\int h(E)\sigma_E dE = \int_{E_t-\delta}^{E_t+\delta} h(E)\sigma_E dE \approx h(E_t)\int \sigma_E dE, \tag{S15}$$

where $h(E)$ is any energy dependent function. With this assumption, the general expression Eq.S2 for Seebeck reduces to Eq.S14 since $\int \sigma_E dE$ and $|-\partial f/\partial E|_{E=E_t}$ from the numerator and denominator cancel out. Note that this approximation can be applied to any functional form of σ_E as long as it is only nonzero within in a narrow energy range $< k_BT$ (see Fig.S3).

The Heikes formula can next be derived by recognizing that the fraction of carriers available in the narrow band or transport energy level is simply related to c, the ratio of the number of occupied states in the band $\int f(E)N(E)dE$ to the total number of states $\int N(E)dE$ (where $N(E)$ is the density of states):

$$c = f(E_t) = \frac{1}{1 + \exp[\frac{E_t - E_F}{k_BT}]}, \tag{S16}$$

which is equivalently $\frac{E_t - E_F}{k_BT} = \ln\left(\frac{1-c}{c}\right)$. Substitution into the Seebeck equation for narrow transport functions (Eq.S14) gives the Heikes formula, Eq.S13.

The conductivity counterpart of Heikes can be obtained by using a useful identity:

$$-\frac{\partial f}{\partial E} = \frac{f(1-f)}{k_BT}, \tag{S17}$$

which, when substituted into Eq.S1 together with Eq.S16 while using Eq.S15, leads to:

$$\sigma = c(1-c)\int \sigma_E dE \equiv c(1-c)\cdot\sigma_M. \tag{S18}$$

σ_M (functioning as a mobility) might be interpreted as an imaginary maximum conductivity[7] when the full transport function is utilized, but $\sigma = \sigma_M$ is inherently not achievable.

We have seen that the Heikes formula assumes a narrow transport function. In band conduction, this assumption is also referred to as the narrow band assumption. In hopping conduction, it is often assumed that one can consider a single transport energy level where all the charge transport occurs[8,9]. This transport energy is a statistical concept, or a virtual energy level where the hopping rate is maximized, which could be considered a narrow transport function assumption. In this sense, the Heikes formula does not necessarily assume localized or delocalized carriers.

1.4 Fritzsche equation

Often, the Heikes formula or Eq.S14 is used to analyze intrinsic semiconductors or wide-gap materials (insulators). This usage could be understood through the work of Fritzsche[10], where the equation for Seebeck coefficient under a general context is given:

$$S = \frac{k_B}{e}\left[\frac{E_t - E_F}{k_B T} + A(\eta)\right]. \tag{S19}$$

This equation looks similar to Eq.S14 with an addition of a dimensionless $A(\eta)$ term. It is seen that when $A(\eta)$ is assumed to be negligibly small, it is likely that a narrow transport function is being considered. $A(\eta)$ is also often considered a constant with respect to η, which is only true when the chemical potential is far below the transport edge ($\eta \ll -1$).

The general form of $A(\eta)$ is readily identified by recognizing $\eta = -\frac{E_t - E_F}{k_B T}$ and comparing with Eq.S2:

$$A(\eta) = \frac{\int \sigma_E \left(-\frac{\partial f}{\partial E}\right)\left(\frac{E}{k_B T}\right) dE}{\int \sigma_E \left(-\frac{\partial f}{\partial E}\right) dE}. \tag{S20}$$

When a transport function of a power form $\sigma_E(E) = \sigma_{E_0}\cdot(E - E_t/k_B T)^s$ is considered, one can compare Eq.S19 with Eq.8 of the main text to notice that $A(\eta)$ is:

$$A(\eta) = \frac{(s+1)F_s(\eta)}{sF_{s-1}(\eta)}, \tag{S21}$$

which is just a result of substituting the power form σ_E into Eq.S20.

It was already identified in Eq.S7 of Section 1.1 that, in the $\eta \ll -1$ limit, $A(\eta) \rightarrow s+1$. In general, $A(\eta)$ is a monotonically increasing function with η as plotted in Fig.S4 where the limitations of considering it small or constant is apparent.

The thermopower of a narrow transport function discussed in Section 1.3, equivalent to $A = 0$, is sometimes applied to intrinsic semiconductors or insulators. Since A is a constant in these materials, one might see satisfactory fittings to experimental data, but quantitative interpretation is valid only if the thermopower is much larger than $\frac{k_B}{e}\cdot A$ (≈ 172 μV/K for $s = 1$).

1.5 Mobility and band transport models

Band conduction equations in terms of mobility and specific scattering mechanisms that are used in inorganic crystalline materials can also be reformulated in terms of $\sigma_E(E)$. Here we demonstrate this translation because it could be valuable for comparing the performance

DOI: 10.1038/NMAT4784

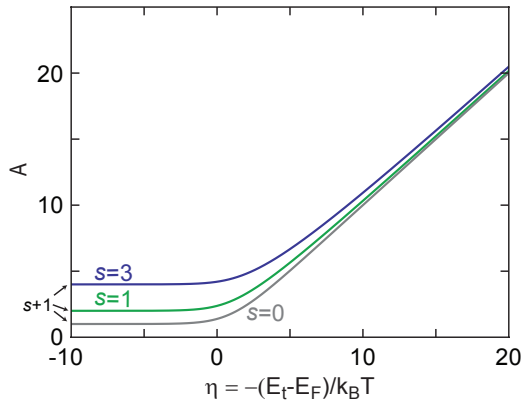

Figure S4: The $A(\eta)$ parameter in Eq.S19, as a function of reduced chemical potential for different transport functions. It is seen that A is only a constant when the chemical potential is far below the mobility or band edge. Contribution of $A = 2$ ($s = 1$ and $\eta \ll -1$) corresponds to a thermopower of ≈ 172 µV/K which is non-negligible in general.

of disordered materials with typical crystalline materials and because one could compare mechanistically different systems on a common phenomenological basis (*i.e.* $\sigma_E(E)$).

Mobility is the most common metric in band transport models. Most types of mobilities derive from the classical Drude relation $\sigma = |e|\, n\mu_d$ where n is carrier concentration and μ_d is drift mobility. For band conductors, the use of μ_d which heavily relies on a clear definition of n is not ambiguous. Unlike non-crystalline systems, the states in a band conductor that allow charge transport and those that do not are clearly delineated.

Even though only the carriers at the chemical potential contribute to transport, the value of n in the classical relation includes all the carriers in the conducting band – even if they are well below the chemical potential, not contributing to conduction. Fortunately, in 3D crystalline semiconductors charge transport is well described with a clearly defined band edge. Like the free electron model, semiconductors can be described with a parabolic dispersion relation, in which case n does scale with σ in the non-degenerate limit.

In a parabolic band with dispersion relation defined by an effective mass, m^*, drift mobility scales with the transport coefficient σ_{E_0}, although it also depends on the effective mass, chemical potential, and temperature:

$$\mu_d = \sigma_{E_0} \cdot \left(\frac{m^*}{m_e}\right)^{-3/2} \cdot \frac{2\pi^2\hbar^3}{e(2m_e k_B T)^{3/2}} \cdot \frac{sF_{s-1}(\eta)}{F_{1/2}(\eta)}, \tag{S22}$$

where m_e is the mass of an electron. In the non-degenerate limit, this relation becomes independent of the chemical potential:

$$\mu_d = \sigma_{E_0} \cdot \left(\frac{m^*}{m_e}\right)^{-3/2} \cdot \frac{2\pi^2\hbar^3}{e(2m_e k_B T)^{3/2}} \cdot \frac{2s\Gamma(s)}{\sqrt{\pi}} \quad (\eta \ll -1). \tag{S23}$$

Figure S5 plots the relation between μ_d and σ_{E_0}.

We next derive these relations and also show how various scattering mechanisms correspond to the s parameter. In semi-classical band conduction for a single effective band (3D, isotropic), $\sigma_E(E)$ corresponds to[2]:

$$\sigma_E(E) = \frac{e^2}{3}\tau(E)v^2(E)N(E), \tag{S24}$$

where $\tau(E)$ is the relaxation time, $v(E)$ is the velocity of the carrier, and $N(E)$ is the density of states. The energy dependence of the relaxation time depends on the scattering mechanisms by

which carriers revert to equilibrium, which can be expressed with a power law:

$$\tau = \tau_0 \cdot \left(\frac{E}{k_B T}\right)^r. \tag{S25}$$

Here τ_0 is a reference relaxation time for carriers at $k_B T$ above the band edge and r is characteristic of the scattering mechanism. Acoustic-phonon scattering ($r = -1/2$; sometimes[11] called $\lambda = 0$ because $\lambda = r + 1/2$) and ionized-impurity scattering ($r = 3/2$) are some of the commonly observed mechanisms.

By using the expression for 3D density of states:

$$N(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2}, \tag{S26}$$

and also $E = m^* v^2/2$ for free carriers, the transport function for band conduction Eq.S24 becomes:

$$\sigma_E = \frac{e(2m_e k_B T)^{3/2}}{3\pi^2\hbar^3} \cdot \mu_0 (\frac{m^*}{m_e})^{3/2} \cdot \left(\frac{E}{k_B T}\right)^{r+3/2}, \tag{S27}$$

where we have introduced the mobility parameter $\mu_0 = \frac{e\tau_0}{m*}$. By comparing to $\sigma_E(E) = \sigma_{E_0} \cdot (E/k_B T)^s$, one can find the correspondence:

$$s \;\rightarrow\; r + \frac{3}{2} \tag{S28}$$

$$\sigma_{E_0} \;\rightarrow\; \frac{e(2m_e k_B T)^{3/2}}{3\pi^2\hbar^3} \cdot \mu_0 (\frac{m^*}{m_e})^{3/2}. \tag{S29}$$

Here we see how acoustic-phonon scattering ($r = -1/2$) and ionized-impurity scattering ($r = 3/2$) correspond to $s = 1$ and $s = 3$, respectively. It is also seen that σ_{E_0} scales with weighted mobility $\mu_0(\frac{m^*}{m_e})^{3/2}$ for a given temperature.

To derive the expression for drift mobility (Eq.S22), we need carrier concentration which can be obtained through:

$$n = \int N(E) f dE = \frac{1}{2\pi^2}\left(\frac{2m^* k_B T}{\hbar^2}\right)^{3/2} \cdot F_{1/2}(\eta). \tag{S30}$$

The drift mobility relation can then be obtained through the Drude relation ($\sigma = |e|\, n\mu_d$) and the conductivity equation (Eq.7 of the main text).

1.6 Spectral conductivity $\sigma_s(E)$ equations

Some authors[10] use a spectral conductivity, which we denote here as $\sigma_s(E)$, that is different than the transport function $\sigma_E(E)$. Spectral conductivity is the contribution to conductivity at each energy for *a given chemical potential* and is zero at values far away from the chemical potential, showing the actual distribution of transport within the spectrum of carrier energy. Because of this definition, spectral conductivity $\sigma_s(E)$ is inherently chemical potential dependent while $\sigma_E(E)$ is not. Spectral conductivity and the transport function can be related through:

$$\sigma_s(E, \eta) = \sigma_E(E) \times \left(-\frac{\partial f(E, \eta)}{\partial E}\right). \tag{S31}$$

It is seen that spectral conductivity has the units of conductivity per energy, whereas the transport function has the units of conductivity. Since $\sigma_s(E)$ is representative only of a given sample (*i.e.* given chemical potential), $\sigma_s(E)$, unlike $\sigma_E(E)$, does not represent the general electronic structure of a family of samples.

$\sigma_E(E)$ is sometimes referred to as the "transport distribution function[12]"; however, it is the spectral conductivity $\sigma_s(E)$ that describes the conductivity "distributed" within the energy spectrum of transport. We therefore use the term "transport function" for $\sigma_E(E)$.

DOI: 10.1038/NMAT4784

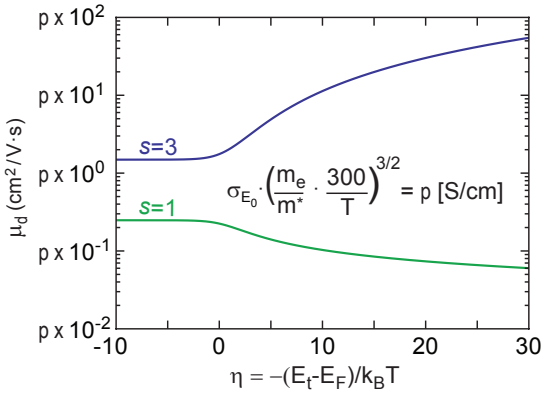

Figure S5: The relation between drift mobility μ_d in band conduction and the transport coefficient σ_{E_0}. μ_d is proportional to σ_{E_0} for a given chemical potential, effective mass, and temperature. It is also seen that, in the non-degenerate limit, μ_d is independent of the chemical potential (carrier concentration) indicating that conductivity is proportional to n, as implied in the Drude relation.

2 Materials quality factor for thermoelectric applications

Using the thermoelectric materials quality factor[13,14], the maximum figure-of-merit zT of an entire family of materials can be determined from measurements of a single sample if it can be assumed σ_{E_0} and s are constant within this family of materials (like the "rigid band assumption").

For a given family of materials, zT is maximized at an optimal chemical potential[15], and the task is to estimate the peak in zT from a non-optimized sample. The figure-of-merit zT that governs the maximum thermoelectric performance is:

$$zT = \frac{S^2\sigma}{\kappa}T = \frac{S^2}{\kappa_l/\sigma T + L}, \tag{S32}$$

where $\kappa = \kappa_e + \kappa_l$ is total thermal conductivity, κ_l is lattice portion of thermal conductivity, κ_e is the electronic portion of thermal conductivity, and L is the Lorenz number that determines the electronic portion of thermal conductivity through the Wiedemann−Franz law: $\kappa_e = L\sigma T$. L can also be calculated from the Boltzmann transport equation[1,2]:

$$L = \left(\frac{k_B}{e}\right)^2 \frac{s(s+2)F_{s-1}(\eta)F_{s+1}(\eta) - (s+1)^2F_s^2(\eta)}{s^2F_{s-1}^2(\eta)}. \tag{S33}$$

It is seen that, for a given transport exponent s, both S and L are only dependent on the reduced chemical potential η. Therefore, by separating out the η dependency from the $\kappa_l/\sigma T$ term in the denominator of Eq.S32, one can isolate the η-independent parameter that only depends on the material properties. By recognizing that $\kappa_l/\sigma T$ has the dimensions of $(k_B/e)^2$, and also that $\sigma = \sigma_{E_0} \cdot sF_{s-1}(\eta)$ (Eq.7 in main text), one can define the materials quality factor B in such a way that it is independent of s and η, dimensionless and an increasing function with zT:

$$\frac{\sigma T}{\kappa_l} \cdot \left(\frac{k_B}{e}\right)^2 = B \cdot sF_{s-1}(\eta), \tag{S34}$$

which leads to[d]:

$$B = \left(\frac{k_B}{e}\right)^2 \frac{\sigma_{E_0}T}{\kappa_l}. \tag{S35}$$

[d]In the original introduction of the concept by Chasmar and Stratton[13], the quality factor B was defined with σ_0 instead of σ_{E_0} by referring to the non-dengenerate limit of conductivity in the form of $\sigma = \sigma_0 \exp(\eta)$. It is seen from Eq.S6 that $\sigma_{E_0} s\Gamma(s) = \sigma_0$. Therefore, the two definitions coincide when $s = 1$ (majority of the inorganic thermoelectric materials), but for $s = 3$ they differ by a factor of $3\Gamma(3) = 6$. Because thermoelectric materials are always optimized near the transport edge rather than in the non-degenerate limit, we believe our definition is more convenient for a general exponent s.

This quality factor B determines the zT vs η curve:

$$zT(B,\eta) = \frac{S^2(\eta)}{\frac{(k_B/e)^2}{B \cdot sF_{s-1}(\eta)} + L(\eta)}, \tag{S36}$$

and thus the maximum achievable zT for a given material (with a fixed σ_E). The B factor also determines the optimum chemical potential (or optimum Seebeck), which can be a useful guide when trying to dope a material towards its optimum (Fig. S6). For example, if $B = 10^{-3}$ in the $s = 3$ case, maximum zT will be on the order of 0.1 and the material will be optimized when the Seebeck coefficient is ≈ 140 μV/K.

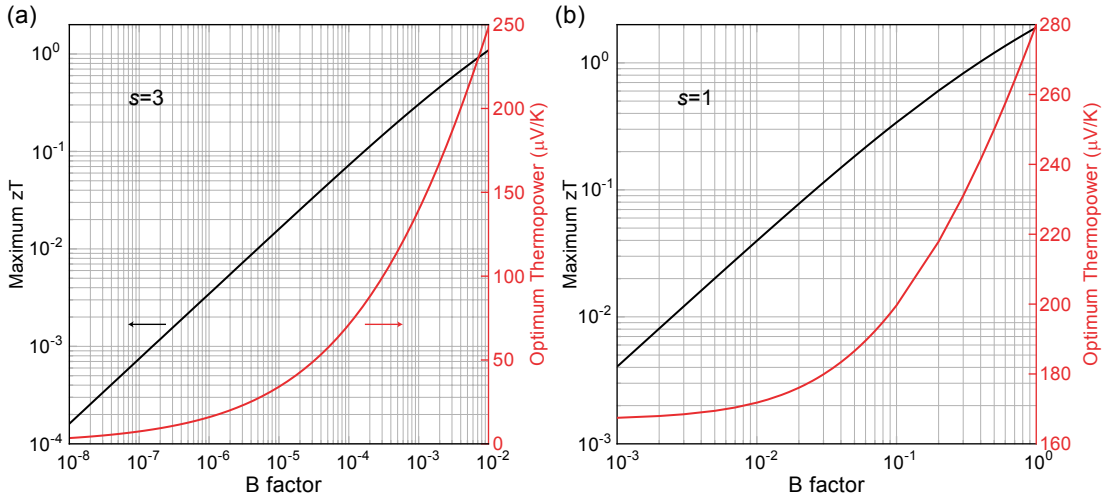

Figure S6: The maximum achievable zT and the optimum thermopower at which the maximum zT is obtained for each B factor. Cases are shown for **(a)** $s = 3$ and **(b)** $s = 1$.

3 The temperature dependence: $\sigma(T)$ and $S(T)$

3.1 Analysis procedure of the temperature dependence

The temperature dependency analysis presented in Fig.2c of the main text is elaborated in Fig.S7. Measured $S(T)$ is converted to $\eta(T)$, which can then be used to extract $\sigma_{E_0}(T)$ from $\sigma(T)$.

3.2 Additional remarks

Thermally activated behavior in electrical conductivity is often a distinguishing feature for non-metallic materials in general. However, the behavior of $\sigma(T)$ by itself is not a strong indication for a specific transport model because similar behavior can result from different origins. For example, it has been shown in section 1.1 that Arrhenius behavior can be seen when the chemical potential is far below the mobility edge. In a different model by Cutler and Mott (nearest-neighbor hopping)[e], Arrhenius behavior results from a hopping term in the transport function[17]. These two origins cannot be distinguished by $\sigma(T)$ alone.

Some transport models explicitly describe $S(T)$ (*e.g.* a power law such as $S \propto T^{1/2}$ in the variable range hopping model, Ref.[3]). This approach is generally useful when the form of density of states is well known, but it seems to be not straightforward for the case of polymers.

[e] Although this work analyzes $S(T)$ together with $\sigma(T)$, their hopping model allows arbitrary energy dependence for the activation energy, and thus does not predict a specific transport function or $S - \sigma$ relation.

DOI: 10.1038/NMAT4784

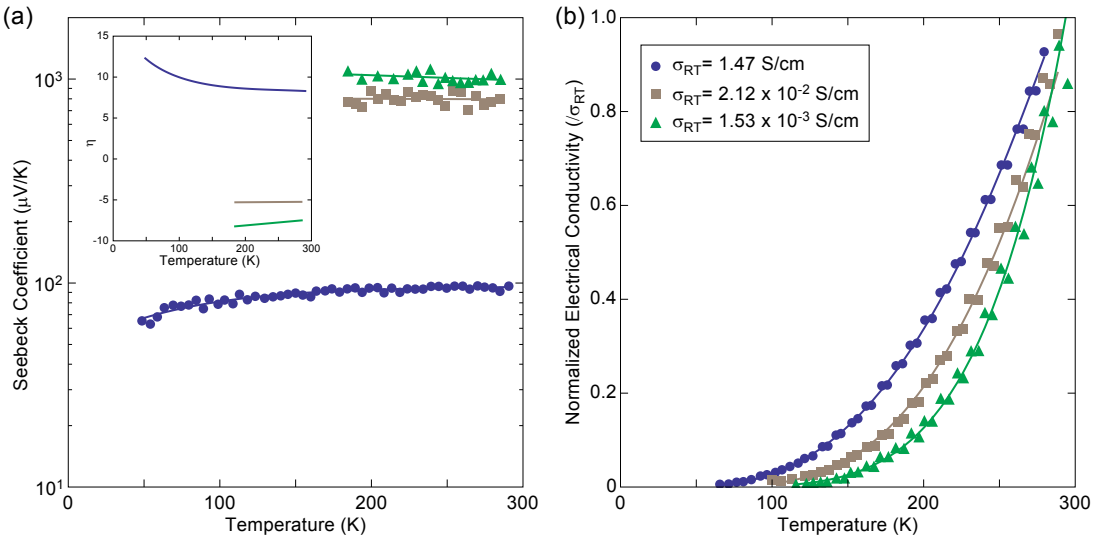

Figure S7: Temperature dependent transport properties of polyacetylene analyzed using the model with $s = 3$. Data points are three sets of paired thermopower and electrical conductivity data from Ref.[16]. Solid lines are from the model fitting with $s = 3$. **(a)** Thermopower is modeled (solid line) by Eq.8 of the main text with a smoothly changing η shown in the inset. The data set includes samples with both $\eta > 0$ and $\eta < 0$. **(b)** The temperature dependent conductivity modeled by taking $\eta(T)$ from (a) and $W_{1/2} = 1.0$ eV obtained from Fig.2c of the main text. W is identical in all three samples.

The thermopower is governed primarily by the reduced chemical potential η, and predicting $S(T)$ is almost equivalent to predicting $\eta(T)$. However, the shift of η in organic semiconductors will be complex in general, because of an unknown distribution of localized states that should be highly sample-dependent. Rather than predicting a general temperature dependency $S(T)$, we find it more helpful to use $S(T)$ as information for analyzing η and the transport function $\sigma_E(E)$.

4 Chemical Abbreviations

Following are chemical abbreviations used in the main text:
poly(3-hexylthiophene) (P3HT);
poly(2,5-bis(3-tetradecylthiophen2-yl)thieno[3,2-b]thiophene) (PBTTT-C_{14});
poly(2,5-bis(thiphen-2-yl)-(3,7-diheptadecantyltetrathienoacene)) (P2TDC$_{17}$-FT4);
tetrafluorotetracyanoquinodimethane (F4TCNQ);
alkyl silane (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-trichlorosilane (FTS);
poly[2,5-bis(2-hexyldecyl)-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-c]pyrrole-1,4-diyl-*alt*-[2,2′:5′,2″-terthiophene]-5,5″-diyl] (PDPP3T);
poly[(4,4′-bis(2-ethylhexyl)dithieno[3,2-b:2′,3′-d]silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl] (PSBTBT);
poly(3-hexylthiothiophene) (P3HTT);
poly(3,4-ethylenedioxythiophene) (PEDOT);
poly(hexyl-3,4-ethyl-enedioxyselenophene) (PEDOS-C_6).

References

1. Ziman, J. M. *Electrons and Phonons* Ch.7 (Oxford Univ. Press, 1960).
2. Fistul, V. I. *Heavily Doped Semiconductors* Ch. 3 (Plenum Press, 1969).
3. Mott, N. F. & Davis, E. A. *Electronic Processes in Non-Crystalline Materials* 2nd ed. (Oxford University Press, 1979).
4. Mott, N. F. The minimum metallic conductivity. *International Reviews in Physical Chemistry* **4,** 1–18 (1985).
5. Glaudell, A. M., Cochran, J. E., Patel, S. N. & Chabinyc, M. L. Impact of the doping method on conductivity and thermopower in semiconducting polythiophenes. *Advanced Energy Materials* **5,** 1401072 (2015).
6. Heikes, R. R. & Ure, R. W. *Thermoelectricity: Science and Engineering* (Interscience Publishers, 1961).
7. Mateeva, N., Niculescu, H., Schlenoff, J. & Testardi, L. R. Correlation of Seebeck coefficient and electric conductivity in polyaniline and polypyrrole. *Journal of Applied Physics* **83,** 3111–3117 (1998).
8. Baranovskii, S. D., Faber, T., Hensel, F. & Thomas, P. The applicability of the transport-energy concept to various disordered materials. *Journal of Physics: Condensed Matter* **9,** 2699 (1997).
9. Schmechel, R. & von Seggern, H. Electronic traps in organic transport layers. *Physica Status Solidi a* **201,** 1215–1235 (2004).
10. Fritzsche, H. A general expression for the thermoelectric power. *Solid State Communications* **9,** 1813–1815 (1971).
11. Andrew, F. M. & Snyder, G. J. in *Materials, Preparation, and Characterization in Thermoelectrics* 1–18 (CRC Press, 2012).
12. Mahan, G. D. & Sofo, J. O. The best thermoelectric. *Proceedings of the National Academy of Sciences* **93,** 7436–7439 (1996).
13. Chasmar, R. P. & Stratton, R. The thermoelectric figure of merit and its relation to thermoelectric generators. *Journal of Electronics and Control* **7,** 52–72 (1959).
14. Goldsmid, H. J. *Introduction to Thermoelectricity* Ch.4 (Springer, 2010).
15. Snyder, G. J. & Toberer, E. S. Complex thermoelectric materials. *Nature Materials* **7,** 105–114 (2008).
16. Park, Y. W. Structure and morphology: relation to thermopower properties of conductive polymers. *Synthetic Metals* **45,** 173–182 (1991).
17. Cutler, M. & Mott, N. F. Observation of Anderson localization in an electron gas. *Physical Review* **181,** 1336–1340 (1969).